

**$^{36}\text{Cl}$ - $^{36}\text{S}$  IN ALLENDE CAIs: IMPLICATION FOR THE ORIGINS OF  $^{36}\text{Cl}$  IN THE EARLY SOLAR SYSTEM.** H. Tang<sup>1\*</sup>, M-C. Liu<sup>1</sup>, K. D. McKeegan<sup>1</sup>, F.L.H. Tissot<sup>2</sup>, and N. Dauphas<sup>3</sup> <sup>1</sup>Ion Probe Group, Department of Earth, Planetary, and Space Sciences, UCLA, Los Angeles CA, 90095; <sup>2</sup>Department of the Earth, Atmospheric and Planetary Sciences, MIT, Cambridge, 02139; <sup>3</sup>The University of Chicago, Origins Lab, Department of Geophysical Sciences and Enrico Fermi Institute, Chicago, IL 60637; ([haolantang@ucla.edu](mailto:haolantang@ucla.edu)).

**Introduction:** Chlorine-36 ( $t_{1/2}=0.3$  Myr) decays to either  $^{36}\text{Ar}$  (98%,  $\beta^-$ ) or  $^{36}\text{S}$  (1.9%,  $\epsilon$  and  $\beta^+$ ). This radionuclide can be produced by either charged particle irradiation [1,2] or stellar nucleosynthesis [3]. Evidence for the prior existence of  $^{36}\text{Cl}$  in the Early Solar System (ESS) comes from radiogenic excesses of  $^{36}\text{Ar}$  [4,5] and/or  $^{36}\text{S}$  [6-9] in secondary phases (e.g., sodalite and wadalite) of ESS materials such as Ca, Al-rich inclusions (CAIs) and chondrules. However, the inferred initial  $^{36}\text{Cl}/^{35}\text{Cl}$  ratios vary over three orders of magnitude among different chondrite constituents ( $5\times 10^{-6}$ - $9\times 10^{-3}$ ) [6-9]. Interestingly, although the initial  $^{36}\text{Cl}/^{35}\text{Cl}$  ratios inferred in previous studies vary widely, all secondary phases bearing evidence for live  $^{36}\text{Cl}$  in the ESS measured so far lack resolvable  $^{26}\text{Mg}$  excesses due to the decay of  $^{26}\text{Al}$  ( $t_{1/2} = 0.7$  Myr), implying that  $^{36}\text{Cl}$  and  $^{26}\text{Al}$  may have been produced by different processes and/or incorporated into ESS solids at different times. Given that secondary phases may have formed late, the  $^{36}\text{S}$  anomalies in secondary phases point to either a very high  $^{36}\text{Cl}/^{35}\text{Cl}$  initial ratio ( $\sim 10^{-2}$ ) in the ESS, or a late irradiation scenario for the local production of  $^{36}\text{Cl}$  ( $> 3$  Myr after CAI formation) [9]. The elevated ESS ratio of  $^{36}\text{Cl}/^{35}\text{Cl} \sim 10^{-2}$  inferred from [9] far exceeds the predictions from any model of stellar nucleosynthesis; therefore, a late irradiation scenario producing  $^{36}\text{Cl}$  is currently the favored idea. In this framework,  $^{36}\text{Cl}$  would be produced in the nebular gas and then incorporated into the CAIs via aqueous alteration, which formed secondary phases.

To further investigate the origin and distribution of  $^{36}\text{Cl}$  in the early solar nebula, we analyzed  $^{36}\text{Cl}$ - $^{36}\text{S}$  systematics in secondary minerals of three fine-grained CAIs and one coarse-grain CAI from Allende.

**Sample description and Method:** The fine-grained Allende CAIs (Curious Marie, AL10S1, and 4321-FG-1) consist of widely-distributed powdery, porous aggregates of sodalite [ $\text{Na}_8(\text{Al}_6\text{Si}_6\text{O}_{24})\text{Cl}_2$ ], nepheline [ $(\text{Na}_3\text{K})\text{Al}_4\text{Si}_4\text{O}_{16}$ ], grossular ( $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ ), and melilite  $((\text{Ca},\text{Na})_2(\text{Al},\text{Mg},\text{Fe}^{2+})[(\text{Al},\text{Si})\text{SiO}_7])$ , suggesting that these CAIs have been intensely altered from their primary mineralogy. Three wadalite grains [ $\text{Ca}_6(\text{Al},\text{Si},\text{Mg})_7\text{O}_{16}\text{Cl}_3$ ] are observed in the coarse-grained CAI (4322-CG-1), occurring as anhedral grains intergrown with grossular replacing melilite. The high chlorine content in sodalite ( $\sim 7$  wt%) and wadalite ( $\sim 12$  wt%) and extremely low sulfur content ( $< 0.01$  wt%) make them ideal minerals for resolving potential  $^{36}\text{S}$  excess due to decay of  $^{36}\text{Cl}$ .

Measurements were performed on the Cameca IMS-1290 at UCLA. Negative S and Cl secondary ions were produced by a 0.6 nA  $\text{Cs}^+$  primary ion beam focused to a  $< 10$   $\mu\text{m}$  spot in mono-collection mode. A long pre-

sputtering time was required ( $> 20$  minutes) to minimize surface S contamination. A mass resolving power of 5,000 was used to resolve interferences from the peaks of interest. Typical count rates of  $^{36}\text{S}$  from the sodalite and wadalite in the CAI samples were 4-10 counts per second. The instrumental mass fractionation was internally corrected by comparison to standards of Balmat pyrite, Canyon Diablo troilite, and CAR 123 pyrite. The transmission was deliberately decreased to minimize the QSA effect (Quasi-Simultaneous Arrival) [10] when measuring the pyrite and troilite standards. Sulfur isotopic ratios were calculated by using total counts due to relatively low  $^{36}\text{S}$  count rate. A systematic offset of 15‰ on the  $^{36}\text{S}/^{34}\text{S}$  ratio was observed on all the standards when normalizing measured  $^{36}\text{S}/^{34}\text{S}$  to the reported value of CDT [11] with corrected  $^{36}\text{S}/^{34}\text{S}_{\text{CDT}} = 0.0034200$ . A terrestrial sodalite ( $^{35}\text{Cl}/^{34}\text{S} = 15,000$ ) was measured to monitor the accuracy of the measurement on  $^{36}\text{S}$  excess.

The bulk  $^{35}\text{Cl}/^{34}\text{S}$  ratio of *Curious Marie* was measured by making 25  $\mu\text{m} \times 25$   $\mu\text{m}$  raster squares on the sample and then averaging the measured  $^{35}\text{Cl}/^{34}\text{S}$  ratios. The signals of  $^{32}\text{S}^-$  and  $^{35}\text{Cl}^-$  were simultaneously collected with L1 (EM) and H2' (FC) with a mass resolution of  $\sim 5,000$ . The relative sensitivity factor (RSF) of  $^{35}\text{Cl}/^{34}\text{S}$  ( $\sim 1.24$ ) used throughout this study was estimated from analyses of NIST 610 glass ( $\text{Cl}/\text{S}=1$ ).

**Result and discussion:** No elevated  $^{36}\text{Cl}/^{35}\text{Cl}$  initial ratio ( $\sim 10^{-2}$ ) was observed in our study. As shown in Fig. 1, no resolvable  $^{36}\text{S}$  excesses were found in the sodalite of AL10S1. Sodalite grains in 4321-FG-1 and wadalite in 4332-CG-1 exhibit resolvable  $^{36}\text{S}$  excesses, giving a  $^{36}\text{Cl}/^{35}\text{Cl}$  ratio of  $\sim 1.6\times 10^{-7}$  and  $\sim 8.3\times 10^{-7}$ , respectively. Assuming an alteration timescale of  $\sim 2.5$  Myr based on  $^{26}\text{Al}$ - $^{26}\text{Mg}$  systematics in secondary phases of CAIs (e.g., [9]), the two CAIs yield an upper limit for the ESS initial  $^{36}\text{Cl}/^{35}\text{Cl}$  ratio  $< 2.7 \times 10^{-4}$ . *Curious Marie* is a U-depleted Allende CAI with highly elevated  $^{235}\text{U}/^{238}\text{U}$ , most likely due to the decay of  $^{247}\text{Cm}$  [12]. Significant excesses in  $^{36}\text{S}$  are clearly resolved in this sample over a large range of  $^{35}\text{Cl}/^{34}\text{S}$  values (from 500 to 20,000). However, the  $^{36}\text{S}$  excesses are uniformly elevated, with a weighted average of  $97\pm 12\%$ , independent of the  $\text{Cl}/\text{S}$  ratio, indicating late closed-system homogenization of the  $^{36}\text{S}$  excesses after  $^{36}\text{Cl}$  became extinct. The  $^{35}\text{Cl}/^{34}\text{S}$  bulk ratio was estimated as  $1145\pm 400$  by averaging 30 raster analyses. The  $^{36}\text{Cl}/^{35}\text{Cl}$  ratio in the bulk of the *Curious Marie* CAI is estimated as  $(1.5\pm 0.6)\times 10^{-5}$ .

The  $^{26}\text{Al}$ - $^{26}\text{Mg}$  systematics has been analyzed in the secondary phases (sodalite and nepheline) of the *Curious Marie* CAI, giving an elevated and uniform  $^{26}\text{Mg}$  excess of

~43‰ and implying a canonical  $^{26}\text{Al}/^{27}\text{Al}$  ratio of  $(6.2 \pm 0.9) \times 10^{-5}$  for the bulk inclusion [13]. To explain this result, an early aqueous alteration event (probably on a small icy body) must have occurred while  $^{26}\text{Al}$  was still at the canonical abundance in the ESS ( $< 0.15$  Myr) [15]. Introduction of  $^{36}\text{Cl}$  into *Curious Marie* likely took place during this event, as any open-system alteration occurring later on would have resulted in a lower than canonical model  $^{26}\text{Al}/^{27}\text{Al}$  ratio for this sample. If so,  $^{36}\text{Cl}$  and  $^{26}\text{Al}$  must have coexisted early in the solar nebula, and the calculated  $^{36}\text{Cl}/^{35}\text{Cl}$  model ratio in *Curious Marie*  $(1.5 \pm 0.6) \times 10^{-5}$  represents the  $^{36}\text{Cl}/^{35}\text{Cl}$  ratio at the time of the early aqueous alteration, thus giving the initial  $^{36}\text{Cl}/^{35}\text{Cl}$  ratio in the ESS to be  $1\text{--}3 \times 10^{-5}$ . This ratio is lower than the upper limit in the ESS inferred in previous studies on sodalities in other CAIs by a factor of ~10 [6,7].

$^{36}\text{Cl}$  can be produced by local irradiation or inherited from stellar sources. The volatile nature of this radionuclide and the need for volatile target nuclides (Cl and K) pose a serious challenge to early in-situ irradiation models [6]. One interpretation is that intense local irradiation could have occurred in a volatile-rich reservoir adjacent to chondrite-accreting regions [9]. Subsequently,  $^{36}\text{Cl}$  was incorporated into secondary, chlorine-rich minerals during parent body alteration. However, this scenario requires an optically thin protoplanetary disk while the Sun was a weak T Tauri star (Class III,  $t \geq 1$  Myr after CAI condensation) and would thus require late aqueous alteration ( $> 1$  Myr). Such late, open-system alteration would remove radiogenic Mg from the inclusion resulting in a lower bulk  $^{26}\text{Al}/^{27}\text{Al}$  ratio ( $^{26}\text{Al}/^{27}\text{Al} \leq 2 \times 10^{-5}$ ), contrary to our results in *Curious Marie*. Hence, we propose that  $^{36}\text{Cl}$  in *Curious Marie* was derived from an external stellar source (e.g., inheritance from the molecular cloud, or a specific stellar source; [3]) along with  $^{26}\text{Al}$ , and accreted into a pre-accretionary icy body. Early aqueous alteration then took place before  $^{26}\text{Al}$  had decayed significantly, and formed  $^{36}\text{Cl}$ -bearing sodalite. The isotopic characteristics of *Curious Marie* indeed suggest that  $^{36}\text{Cl}$  and  $^{26}\text{Al}$  could have been co-incorporated into secondary minerals. However, our observation does not rule out the presence of  $^{36}\text{Cl}$  due to late spallation as inferred in the secondary minerals from other CAIs and chondrules.  $^{26}\text{Al}$ - $^{26}\text{Mg}$  *in situ* analyses in the secondary phases of AL10S1, 4332-CG-1, and 4321-FG-1 will be done in the near future to quantify the timescale of aqueous alteration in these objects.

**References:** [1] Leya et al., (2003) *ApJ* 594, 605-616. [2] Gounelle et al., (2006) *ApJ* 640, 1163-1170. [3] Wasserburg et al., (2006) *Nuclear Physics A* 777, 5-69. [4] Murty et al., (1997) *ApJ* 475, L65-L68. [5] Turner et al., (2013) *GCA* 123, 358-367. [6] Lin et al., (2005) *PNAS* 102, 1306-1311. [7] Hsu et al., (2006) *ApJ* 640, 525-529; [8] Ushikubo et al., (2007) *MAPS* 42, 1267-1279. [9] Jacobsen et al., (2011) *ApJ* 731, L28-L34. [10] Slodzia et al., (2004) *Applied Surface Science* 231, 874-877. [11] Ding et al (2001) *GCA* 65, 2433-2437. [12] Tissot et al., (2016) *Science advances* 2, p.e1501400 [13] Tang et al., (2016) *LPS XLVII* #2539. [14] Tang et al, *GCA*, in Revision.

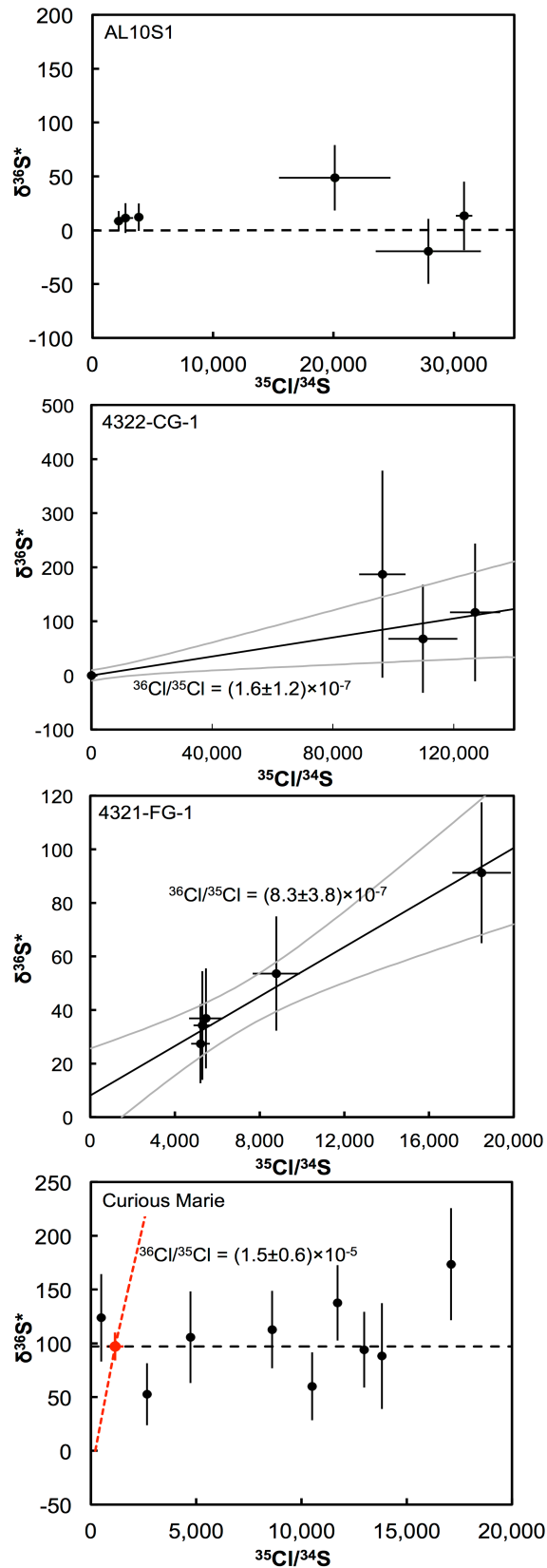


Figure 1.  $^{36}\text{Cl}$ - $^{36}\text{S}$  systematics in Allende CAIs. In *Curious Marie*, red dash line reflects the model  $^{36}\text{Cl}/^{35}\text{Cl}$  ratio based on the average  $\delta^{36}\text{S}^*$  and bulk  $^{35}\text{Cl}/^{34}\text{S}$  ratio.